Entropy and entropic forces

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Focus question

- Biological question: if energy is always conserved, how can some devices be more efficient than others?
- Physical idea: Order controls when energy can do useful work. Order is not conserved.

2

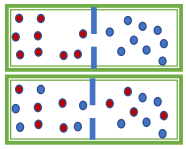
What are the fundamental principles of equilibrium?

Mechanics
$\Sigma_i F_i = -\Sigma_i \nabla U_i = 0$
minimize energy

Thermodynamics
maximize entropy
(minimize F or G)

particle number

identical, coloured, *dU=0*



dS>0, $\mu_1 = \mu_2$

The two principles are related by TDI

$$dU = TdS - PdV + \mu dN$$
$$dH = TdS + VdP + \mu dN$$
$$dF = -SdT - PdV + \mu dN$$
$$dG = -SdT + VdP + \mu dN$$
$$S = -\left(\frac{\partial G}{\partial T}\right)_{N,P} = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

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Entropic force

- $f = -\frac{dF}{dL}$ $\qquad P = \left(\frac{\partial F}{dV}\right)_{N,T}$
- Entropic force is a derivative of a free energy

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What is the chemical potential?

From

$dU = TdS - PdV + \mu dN$

$dH = TdS + VdP + \mu dN$

$dF = -SdT - PdV + \mu dN$

$dG = -SdT + VdP + \mu dN$

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Most useful definitions

F=U-TS	energy to create a system minus the energy from the environment
G=U+PV-TS	energy to create a system and make room for it minus the energy from the environment

OK, but how do we calculate or measure this?

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Chemical potential of ideal gas

(thermodynamics)

Ideal gas: $PV = NkT$

expression for μ: $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

We need some relation between energies, *G* or *F* and *P,V,N,T*

TDI (*F*): $dF = -SdT - PdV + \mu dN$

TDI (*G*): $dG = -SdT + VdP + \mu dN$

=> at constant T & N: $dG = VdP, \quad dF = -PdV$

$$dG = VdP = \frac{NkT}{P}dP$$

$$\int dG = G - G_0 = NkT\int\frac{dP}{P} = NkTln\frac{P}{P_0}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu_0 + kTln\frac{P}{P_0}$$

$$dF = -PdV = \frac{NkT}{V}dV$$

$$\int dF = F - F_0 = -NkT\int\frac{dV}{V} = -NkTln\frac{V}{V_0}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu_0 - kTln\frac{V}{V_0} = \mu_0 + kTln\frac{P}{P_0}, \quad \left(\frac{V}{V_0} = \frac{P_0}{P}\right)$$

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Chemical potential of ideal gas

(stat. mech. of quantum ideal gas)

Helmholtz free energy of quantum ideal gas:

$$F_N(T,V) = -NkT\left[ln\left(\frac{V}{Nv_Q}\right)+1\right]$$

The chemical potential $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

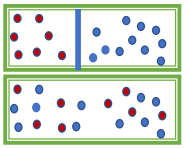
$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left[ln\left(\frac{V}{Nv_Q}\right)+1\right] + NkT\left[\frac{dlnN}{dN}\right]$$

$$\mu = -kTln\left(\frac{V}{V_0}\right),\ V_0 = Nv_Q, \qquad n_Q = v_Q^{-1}$$
$$\mu = kTln\left(\frac{n}{n_Q}\right),\quad n = \frac{N}{V}$$
$$\mu = kTln\left(\frac{P}{P_0}\right),\quad P_0 = n_QkT$$

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Chemical potential of ideal mixtures

V_1 V_2
N_1 N_2
$T_1 = T_2$
$P_1 = P_2$ => $\mu_1^0(P,T) = \mu_2^0(P,T)$



$\mu = \mu_0 - kTln\frac{V}{V_0}$

Remove wall: $V=V_1+V_2$

$$\Delta\mu_1 = -kTln\frac{V_1+V_2}{V_1}$$

$$\frac{V_1+V_2}{V_1} = \frac{N_1+N_2}{N_1} = \frac{1}{x_1}$$

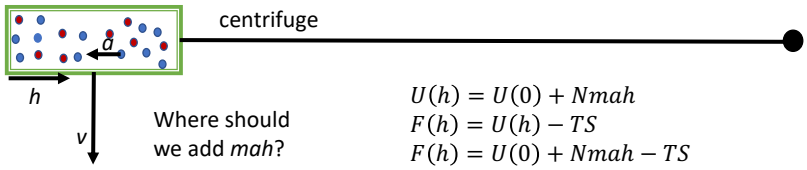
$$\Delta\mu_1 = kTlnx_1$$

$$\mu_i(P,T,x_i) = \mu_i^0(P,T) + kTlnx_i$$

Ideal mixture:
$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1+V_2}$
is independent of mixture composition

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Potential energy and the chemical potential



Where should we add *mah*?

$$U(h) = U(0) + Nmah$$
$$F(h) = U(h) - TS$$
$$F(h) = U(0) + Nmah - TS$$
$$F(h) = F(0) + Nmah$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu(0) + mah$$
$$\mu_{tot} = \mu_{int} + \mu_{ext}$$

Barometric pressure: Can we use this to calculate *p(z)*?

equilibrium: $\mu(z) = \mu_0 = \mu_0 + kTln\frac{P(z)}{P_0} + mgz$

=> $\frac{P(z)}{P_0} = e^{-mgz/kT} = e^{-z/z_c}$

$z_c = kT/mg$

Nitrogen (*m*=28) z_c=8.5km, Oxygen (*m*=32) z_c = 7.4 km, Mount Everest: *P = 0.37 P(0)*

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Boltzmann-statistics

- Reservoir + small system => NVT for the small
- Probability for a state i, ε_i; $E_R=E_0-\varepsilon_i$.
- $P(i) = C\ \Omega_R(E_0-\varepsilon_i)$, multiplisity of the reservoir
- $\varepsilon_i << E_0$, expand

- $P(i) = \exp(-\varepsilon_i/kT)/Z$ Boltzmannfactor

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Boltzman probabilities: The probability for a system S described by N, V, T, to be in a state i with energy ϵ_i is given as

$$P(\epsilon_i) = \frac{1}{Z} e^{-\epsilon_i/kT} \ , \qquad (7.17)$$

where the system is *in equilibrium.*

Partition function: The sum $Z = Z(N, V, T)$ is called the partition function. The sum is over *all the states* i of the system:

$$Z(N, V, T) = \sum_i e^{-\epsilon_i/kT} \ . \qquad (7.18)$$

The **average** of a quantity Q_i, which depends on the state i of a canonical system with given N, V, T, is:

$$\overline{Q}_i = \sum_i P(i)\, Q_i = (1/Z) \sum_i Q_i\, e^{-\epsilon_i/kT} \qquad (7.20)$$

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Two-state system

Two-state systems Here's an immediate example. Suppose the small system has only *two* allowed states, and that their energies differ by an amount $\Delta E = E_2 - E_1$. The probabilities to be in these states must obey both $P_1 + P_2 = 1$ and

$$\frac{P_1}{P_2} = \frac{\mathrm{e}^{-E_1/k_\mathrm{B}T}}{\mathrm{e}^{-(E_1+\Delta E)/k_\mathrm{B}T}} = \mathrm{e}^{\Delta E/k_\mathrm{B}T}, \qquad \text{simple 2-state system.} \qquad (6.24)$$

Solving, we find

$$P_1 = \frac{1}{1+\mathrm{e}^{-\Delta E/k_\mathrm{B}T}} \ , \quad P_2 = \frac{1}{1+\mathrm{e}^{\Delta E/k_\mathrm{B}T}}. \qquad (6.25)$$

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Protein folding

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Reversible Unfolding of Single RNA Molecules by Mechanical Force

Jan Liphardt[1,*], Bibiana Onoa[1], Steven B. Smith[2], Ignacio Tinoco Jr.[1], Carlos Bustamante[1,2,*]

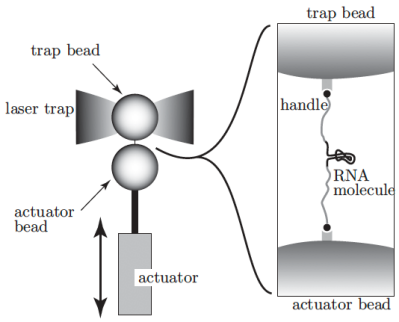
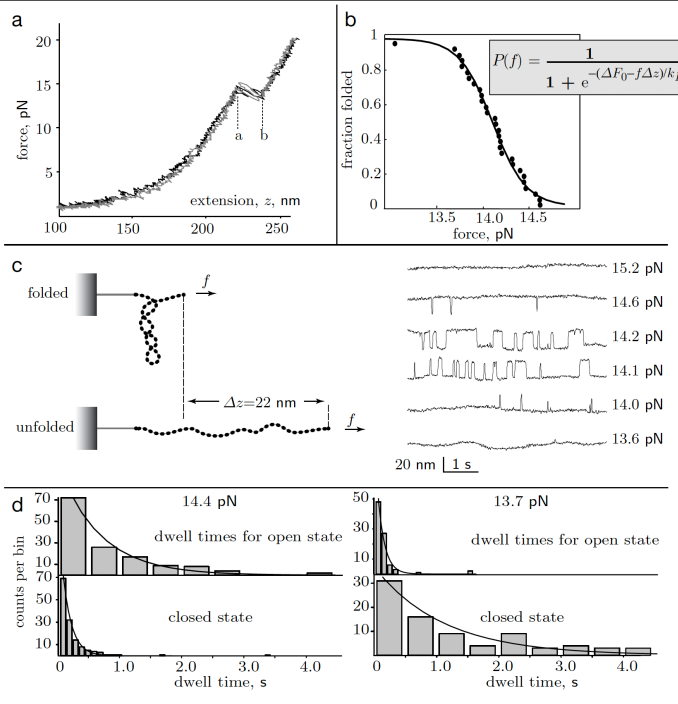
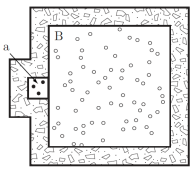


Figure 6.9: (Schematic.) Optical tweezer apparatus. A piezo-electric actuator controls the position of the bottom bead. The top bead is captured in an optical trap formed by two opposing lasers, and the force exterted on the polymer connecting the two beads is measured from the change in momentum of light that exits the optical trap. Molecules are stretched by moving the bottom bead vertically. The end-to-end length of the molecule is obtained as the difference of the position of the bottom bead and the top bead. *Inset:* The RNA molecule of interest is coupled to the two beads via molecular "handles." The handles end in chemical groups that stick to complementary groups on the bead. Compared to the diameter of the beads (≈ 3000 nm), the RNA is tiny (≈ 20 nm). [Figure kindly supplied by J. Liphardt.]

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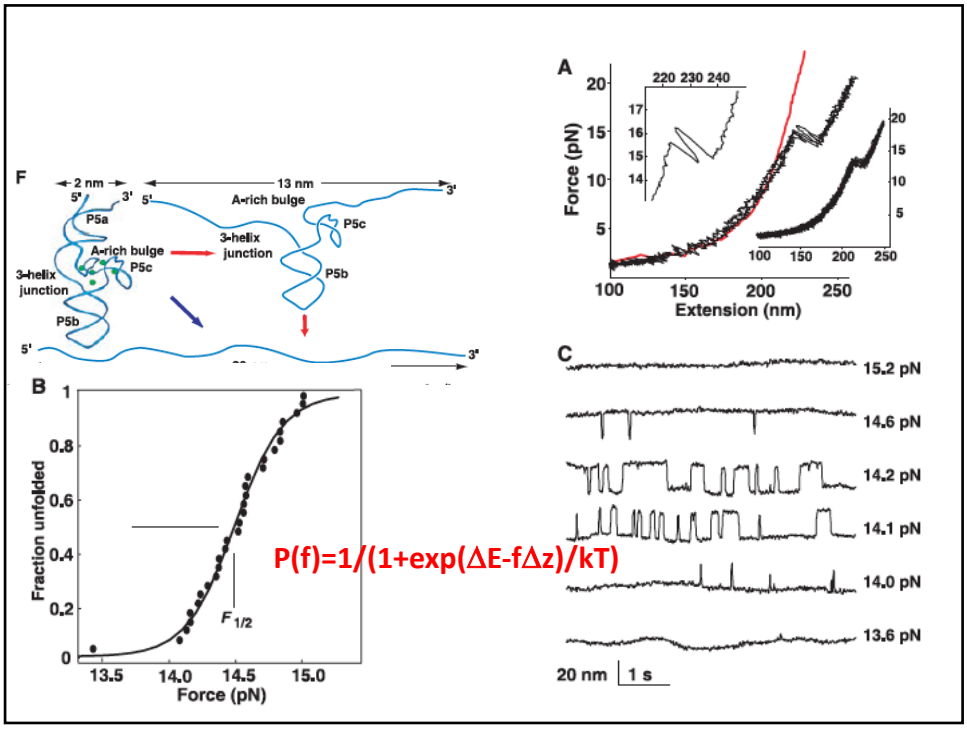




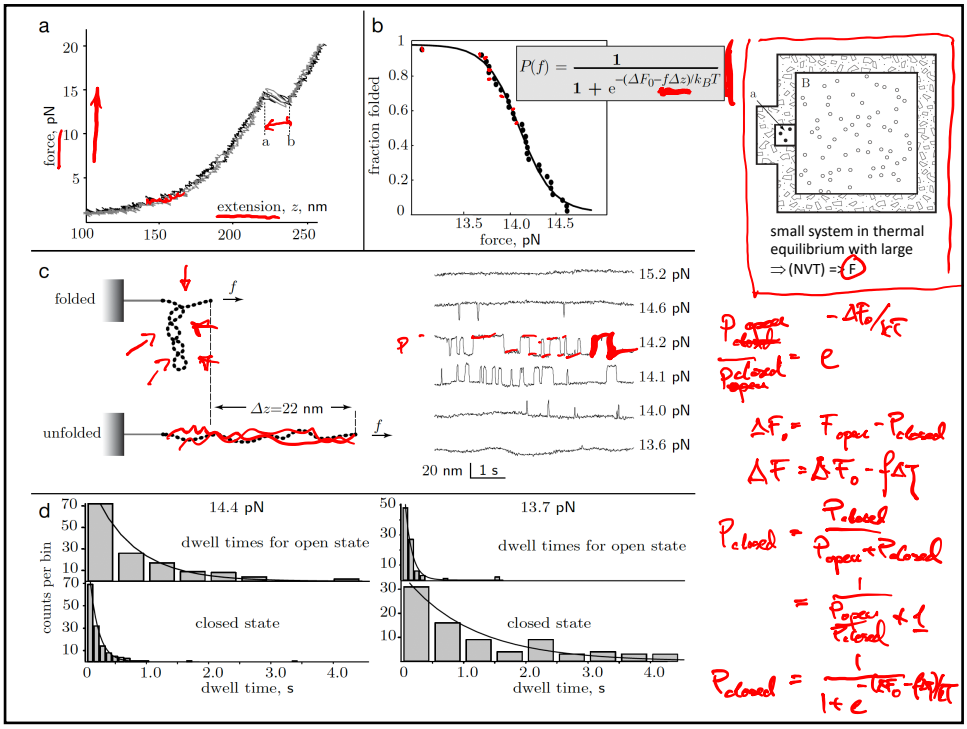
small system in thermal equilibrium with large
⇒ (NVT) => F

What is the most important information to arrive to figure b?

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F
2 nm
13 nm
A-rich bulge
P5a
P5c
3-helix junction
P5b
A
Force (pN)
Extension (nm)
B
Fraction unfolded
$F_{1/2}$
Force (pN)
C
15.2 pN
14.6 pN
14.2 pN
14.1 pN
14.0 pN
13.6 pN
20 nm
1 s
P(f)=1/(1+exp(ΔE-fΔz)/kT)

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a
force, pN
extension, z, nm
b
fraction folded
force, pN
$P(f) = \frac{1}{1 + e^{-(\Delta F_0 - f\Delta z)/k_B T}}$
small system in thermal equilibrium with large
⇒ (NVT) ⇒ F
c
folded
unfolded
Δz=22 nm
f
15.2 pN
14.6 pN
14.2 pN
14.1 pN
14.0 pN
13.6 pN
20 nm
1 s
d
14.4 pN
13.7 pN
dwell times for open state
closed state
counts per bin
dwell time, s

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Problems

6.6 *Polymer mesh*

Recently D. Discher studied the mechanical character of the red blood cell cytoskeleton, a polymer network attached to its inner membrane. Discher attached a bead of diameter 40 nm to this network (Figure 6.12a)). The network acts as a spring, constraining the free motion of the bead. He then asked, "What is the stiffness (spring constant) of this spring?"

In the macroworld we'd answer this question by applying a known force to the bead, measuring the displacement Δx in the x direction, and using $f = k\Delta x$. But it's not easy to apply a known force to such a tiny object. Instead Discher just passively observed the thermal motion of the bead (Figure 6.12b). He found the bead's root-mean-square deviation from its equilibrium position, at room temperature, to be $\sqrt{\langle(\Delta x)^2\rangle} = 35\,\text{nm}$, and from this he computed the spring constant k. What value did he find?

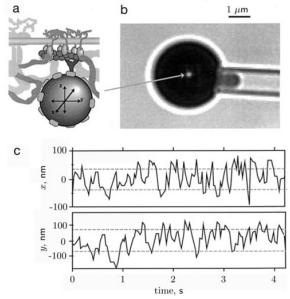


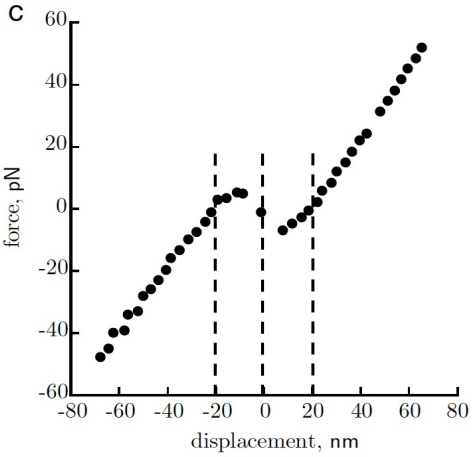
Figure 6.12: (Schematic; optical micrograph; experimental data.) (a) Attachment of a single fluorescent nanoparticle to actin in the red blood cell cortex. (b) The red cell, with attached particle, is immobilized by partially sucking it into a micropipette (right) of diameter 1 μm. (c) Tracking of the thermal motion of the nanoparticle gives information about the elastic properties of the cortex. [Digital image kindly supplied by D. Discher; see Discher, 2000.]

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6.7 *Inner ear*

A. J. Hudspeth and coauthors found a surprising phenomenon while studying signal transduction by the inner ear. Figure 6.13a shows a bundle of stiff fibers ("stereocilia") projecting from a sensory cell. The fibers sway when the surrounding inner-ear fluid moves. Other micrographs (not shown) revealed thin, flexible filaments ("tip links") joining each fiber in the bundle to its neighbor (wiggly line in the sketch, panel (b)).

The experimenters measured the force-displacement relation for the bundle by using a tiny glass fiber to poke it. A feedback circuit maintained a fixed displacement for the bundle's tip, and reported back the force needed to maintain this displacement. The surprise is that the experiments gave the complex curve shown in panel (c). A simple spring has a stiffness $k = \frac{df}{dx}$ that is constant (independent of x). The diagram shows that the bundle of stereocilia behaves as a simple spring at large deflections, but in the middle it has a region of *negative* stiffness!



· at one end of the tip
loor was effectively a
.
: can wander at will,
plied force the curve
we will never observe

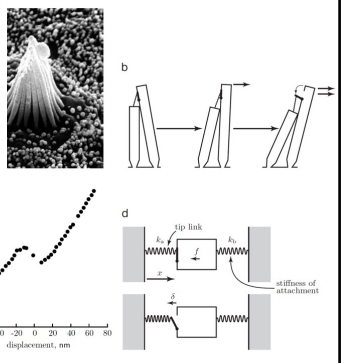


Figure 6.13: (Scanning electron micrograph; diagram; experimental data; diagram) (a) Bundle of stereocilia projecting from an auditory hair cell. [Digital image kindly supplied by A. J. Hudspeth.] (b) Pushing the bundle to the right causes a relative motion between two neighboring stereocilia in the bundle, stretching the tip link, a thin filament joining them. At large enough displacement the tension in the tip link can open a "trap door." (c) Force that must be applied to a hair bundle to get various displacements. Positive values of f correspond to forces directed to the left in (b); positive values of x correspond to displacements to the right. [Data from Martin et al., 2000.] (d) Mechanical model for stereocilia. The left spring represents the tip link. The spring on the right represents the stiffness of the attachment point where the stereocilium joins the main body of the hair cell. The model envisions N of these units in parallel.

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